The Tetrahedral Motif in Metal Structures

THE TETRAHEDRAL MOTIF IN METAL STRUCTURES

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Abstract

F.C. Frank's demonstration of the stability of the icosahedral configuration to either of the close packed ones in thirteen-atom clusters of mutually attracting hard spheres renewed interest in the occurrence of tetrahedral configurations in metal alloy structures. This paper reviews some of these developments.

Consider the packing of mutually attracting, by central forces of hard spheres. In two dimensions the densest, and presumably lowest energy, packing unit is an equilateral triangular configuration which, when replicated, can fill space to form a hexagonal structure.

In contrast, in three dimensions, the configuration with lowest energy and highest density is a regular tetrahedron which, by itself, cannot be replicated to fill space and form a close-packed crystalline structure. The problem then arises of how these tetrahedral configurations, energetically preferred at short range, are incorporated in, or affect, three-dimensional structures. In this paper, various ways of including tetrahedral configurations into liquid, glass, and crystalline structures will be reviewed. Some excellent earlier treatments of this topic are:

M. Hoare [1]

F.C. Frank and J. Kasper [2]

F. Yonazawa [3]

J.F. Sadoc and R. Mosseri [4]

L. Bartell [5]

D.R. Nelson and F. Spaepen [6]

The Science of Alloys for the 21st Century:
A Hume-Rothery Celebration
Edited by E.A. Turchi, R.D. Shull and A. Gonis
TMS (The Minerals, Metals & Materials Society), 2000

Hume-Rothery-Anderson model would predict. The melting temperature of the ordered intermetallic phase with composition ~Au4Si is only 5°K below that of the actual eutectic.

Deposition from the pure metal vapor or dilute solution onto cold substrates might, initially, result in the formation of icosahedral, or other polytetrahedral, clusters (these have been labeled "amorphons"). These amorphons would continue to enlarge, and upon mutual impingement form a microquasicrystalline or, perhaps, a glassy structure. There is the intriguing possibility that below a certain thickness a quasicrystalline structure might be preferred, thermodynamically, to a microcrystalline one at the same atomic density. However, we know of no experimental evidence of a direct transformation from a micro-crystalline to a quasi-crystalline state.

A considerable number of metal alloys form structures in which icosahedral groups of atoms, as defined by Dirichlet constructions, are prominent components of the overall structure. Kasper also noted other coordination polytetrahedra which often appear in these structures. Frank and Kasper then examined these phases and outlined the general principle for inclusion of tetrahedral configurations in alloy structures. These alloys have come to be known as "Frank-Kasper phases".

Since icosahedral configurations appear to be important components of liquid structure, it seems that their resistance to nucleation of crystals with major polytetrahedral groups might be much lower than that to simple close-packed structures. This comparison can be made roughly in terms of the scaled, with thermodynamic melting temperature, T_m, undercooling at the onset of measurable crystal nucleation, $(T_m-T_N)/T_m = a$. For most pure metals, a is of order 0.2 to 0.25. At this time, information on those metals in which polytetrahedral groupings are prominent in their structures is rather sparse. However, recent studies at the Institut für Raumsimulation in Cologne by D. Holland-Moritz, D.M. Herlach and their coworkers, have indicated that a, for phases with major icosahedral or other polytetrahedral configurations in their structures, do indeed exhibit a values (~0.10) substantially below those with crystalline close-packed structures. The Cologne results were obtained by observation of droplets which were levitated electromagnetically. Earlier observations by Bendersky and Ridder [9] on the formation

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ordinarily deep eutectic at
rature is roughly 540°C
accord with what the

Hume-Rothery-Anderson model would predict. The melting temperature of the ordered intermetallic phase with composition ~Au_4Si is only 5°K below that of the actual eutectic.

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of quasicrystals from suspended droplets of Al-Mn alloy indicated in the condensed structure an extremely high concentration (~10^{18}/cm^3) of microquasicrystallites.

This research was sponsored by NASA grant NAG8-1256.

References

[1] Hoare, M.R., J. Non-Crystalline Solids, 31, 157 (1978).

[2] Frank, F.C. and J. Kasper, Acta Cryst., 11, 184 (1958); 12, 483 (1959).

[3] Yonazawa, F., Solid State Physics, 45, 179 (1991).

[4] Sadoc, J.F. and R. Mosseri, *Geometrical Frustration* (Cambridge University Press, 1999).

[5] Bartell, L., Ann. Rev. Phys. Chem. 49, 43 (1998).

[6] Nelson, D.R. and F. Spaepen, Solid State Physics, 42, 1 (1989).

[7] Hoare, M.R. and P. Pal, Adv. Phys., 20, 161 (1971).

[8] Hume-Rothery, W. and E. Anderson, Phil. Mag., 5, 383 (1960).

[9] Bendersky, L.A. and S.D. Ridder, J. Mater. Res., 1, 405 (1986).

PHYSICS AND METALLU

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The basic factors governi
reviewed and discussed in the
development of complex multico
characteristic of conventional cast
surveyed. The key kinetic and th
these systems are outlined. Fina
liquid/crystal mixtures to produ
unique properties is described.

Glass Formation in M

The early work of Tur
demonstrated that a thermodynar
local fluctuation in the liquid in c
analysis of the rate of crystal nuc
rate formation of stable crysta
depends on the height of nuclea
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(1) R = nucleation rate/ur

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decreases with undercooling. In
Turnbull:

(2) $W \sim (16\pi/3)\gamma^3/\Delta g^2 \sim$

where Δs_f is the specific entr
crystallization (both per unit v
as a constant), and T_m the me
approximation).
The rate of atomic rearrangem
coefficient in the melt and is
through the Stokes-Einstein rel
dating the early 20th century, ha
temperature dependence: